THE DIELECTRIC PROPERTIES OF ROSIN

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ABSTRACT. The dielectric properties of w. w. rosin have been measured over a wide range of temperature and frequency, viz., from 20°C to 150°C and from 1 kc/s to 500 kc/s. Within the temperature range of investigation rosin behaves as a typical polar rosin in the anomalous dispersion range. The range of dispersion is wide and this may be explained from the distributed relaxation times of its polar units. With the help of melt viscosity data of this resin the size of its rotating unit has been calculated following Debye's relations and the calculated radius comes out to be 4.6 Å.

INTRODUCTION

It has been recently observed (Sen and Bhattacharya, 1958) that ester gum, which is the glycerol ester of rosin, behaves as a typical polar resin. Its loss curve is a typical absorption curve but owing to its somewhat large molecule it has a distributed range of relaxation time due to which it has a wide range of dispersion as well as a diminished value of the dielectric loss. The application of Stokes' law for estimation of the radius of the rotating unit has revealed that probably a part of the molecule only rotates and the ester gum molecule as a whole does not take part in the orientation. Chemically speaking ester gum is mainly glyceryl tri-abietate i.e., glycerol ester of abietic acid, the chief constituent of rosin. It is of interest, therefore, to study the dielectric properties of rosin, the raw material for ester gum in order to account for its dielectric loss and to obtain an idea of the size of the rotating unit in this case.

There are two types of rosin available at present—one is "gum rosin" obtained from the resinous exudation of the pine tree and the other is "wood rosin" extracted from stumps of rosin-bearing wood. Nearly the entire production of Indian rosin is of the gum type. Though extensive work has been done in America on the various physical and chemical properties of rosin produced there, very little information is available about Indian rosin. Rau and Simonsen (1924) however have shown that the abietic acid isolated from rosin derived from Indian Pinus Longifolia is identical in all respects with the acid present in the rosin from American Pinus Palustris.

THEORETICAL

The relation between the dielectric constant ϵ' and loss factor ϵ'' of a substance which exhibits the phenomenon of absorption is expressed as

$$\epsilon'' = \epsilon' \tan \delta$$

where tan δ is the power factor of the condenser filled with the given dielectric material and δ is its loss angle. The dielectric constant ϵ' and the power factor tan δ of the condenser may be determined in the usual manner and the dielectric loss may be computed.

Now, the current in phase with the voltage in a condenser having dielectric loss is

$$I_r = I \tan \delta = \omega C V \tan \delta$$
$$= 2\pi f C V \frac{\epsilon''}{\epsilon'} .$$

But the value of C for a parallel plate condenser of area A and the dielectric thickness d is given by

$$C = \frac{A \times \epsilon'}{4\pi d \times 9 \times 10^{11}} \text{ farads.}$$

Therefore substituting this value of C, we have

$$I_r = \frac{fAV\epsilon''}{18 \times 10^{11} \times d}$$

Again, if K_t is the total conductance of this condenser, then

$$I_r = \frac{AVK_t}{d}$$

Therefore,

$$\epsilon'' = \frac{18 \times 10^{11} \times K_t}{f}$$

But $K_t = K_0 + K$, where K_0 and K are the d.c. and a.c. conductance respectively. Hence pure a.c. loss would be

$$\epsilon'' = \frac{18 \times 10^{11} (K_t - K_0)}{f}$$

EXPERIMENTAL

Apparatus :—The bridge, oscillator and amplifier null detector employed for capacity and power factor measurements in the present investigation were the same as reported previously (Sen and Bhattacharya, 1958) for ester gum. The cell used was also the same.

Material :—The sample of rosin used was of the "water white" commercial grade and was obtained from Napier Paint Works Ltd., Calcutta. The softening point of the sample determined by the mercury surface method was 67°C.

Method of procedure :—The procedure followed for the measurement of capacity and power factor as well as for filling up the experimental cell has already been described in some detail elsewhere (Sen and Bhattacharya, 1958).

D.c. conductivity was measured at different temperatures using the same cell. The values of d.c. conductance reported here were obtained after 2 minutes of electrification. For this measurement direct deflection method was used employing a precision universal shunt and a sensitive galvanometer. The viscosity of the sample was determined using Lee's modified viscometer (Lee, 1934) as reported previously (Sen and Bhattacharya, 1957).

DISCUSSION

The results of measurements of power factor tan δ, the dielectric constant ϵ' and the dielectric loss factor ϵ'' for various temperatures and frequencies are shown graphically in figures 1, 2 and 3. These curves, it may be seen, indicate

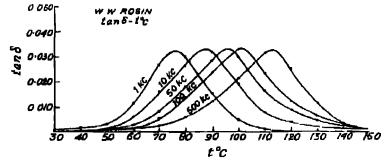

Fig. 1.

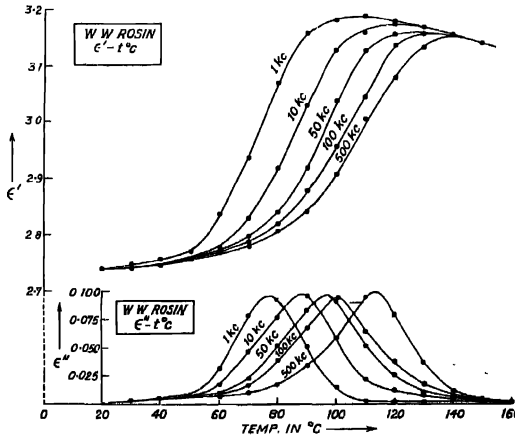

Fig. 2. and Fig. 3.

the characteristics of a typical polar resin in the anomalous dispersion range. Almost similar curves were obtained in our previous investigation on ester gum and the general interpretations given in our previous paper (Sen and Bhattacharya, 1958) as regards its behaviour at different temperatures and frequencies hold good in the present case also. A detailed discussion on the electrical behaviour of this resin is therefore omitted here.

The power factor as well as the dielectric loss curves of rosin begin to rise from about 40°C. The dielectric constant is also very small below this temperature. The maximum value of power factor remains practically the same for all frequencies and is about 0.033. The region of temperature within which the power factor peaks are distributed is about 37°C, the peak for 1 kc/s occurring at 76°C while that for 500 kc/s occurring at 113°C.

The values of dielectric constant and power factor reported here are in good agreement with those mentioned by Clare (1949) or by Kitchin and Muller (1928), although the samples used by these investigators are of different origin. It would be reasonable to think therefore that the basic constituent of rosin primarily responsible for its dielectric behaviour is the same in all samples irrespective of different methods of processing and different countries of origin.

As is well known most of the resins are characterised by a band of distributed relaxation time instead of a single one as demanded by Debye's orginal theory. Various workers have demonstrated the effect of such distributed relaxation times and have indicated the mechanism of such distribution of relaxation times in resins. Fuoss and Kirkwood's (1941) theory which accounted for the existence of such bands in high polymers can be used to calculate this factor of distribution in resins. Yager (1936) has also shown from theoretical considerations that the

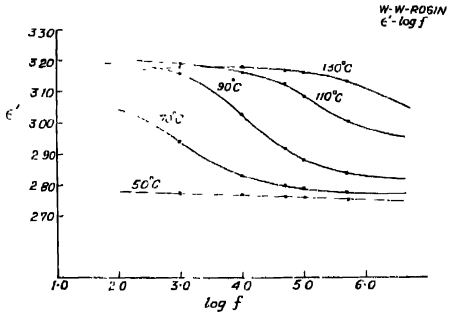

Fig. 4

effect of distributed relaxation times in a polar resin is to diminish the maximum loss factor ϵ_m'' and also to widen the dispersion band. These two phonomena

often serve as an indication of the existence of distributed relaxation times in the molecule. In this case the calculated value of ϵ_m'' at 90°C, for example, comes

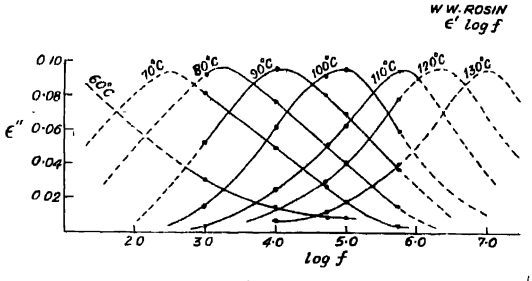

Fig. 5.

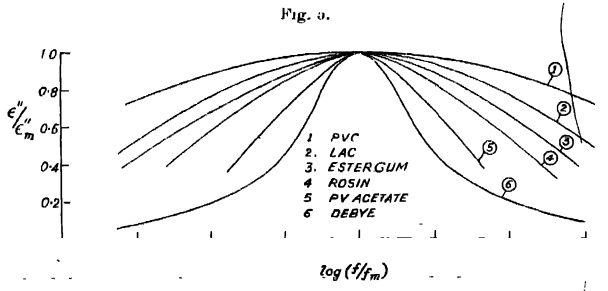

Fig. 6.

out to be 0.20 and the observed maximum loss factor (from figure. 5) is 0.096 i.e., about half of the theoretical value. The dispersion band also spreads over a wide range—for at least 5 or 6 decades of frequency.

From both these considerations, viz., the diminished value as well as a wide-spread dispersion range, a distributed range of relaxation time of the rosin molecule suggests itself. It can be seen also from a study of the bluntness or flatness of the $\frac{\epsilon''}{\epsilon_m''}$ vs. $\frac{f}{f_m}$ curve for this sample compared with the Debye graph in figure 6. A comparative study of the degree of such an effect in different substances may be made by plotting such curves in one graph where blunter curves will indicate greater effect of distributed relaxation times.

In the case of a liquid where Stokes' law is applicable the relaxation time τ is given by the relation, due to Debye, viz,

$$\tau = \frac{4\pi\eta a^3}{KT}$$

where η = coefficient of viscosity and a = radius of the rotator,

This simple relation of Debye has been found to hold good in cases of liquids having molecules of smaller size and simpler shape and proper values of molecular radii are obtained by putting the macroscopic value of viscosity for η in it.

But the propriety of substituting the macroscopic value of viscosity for the coefficient of internal friction in the above relation in cases of resins having larger and more complex molecular structure is often open to criticism.

In fact, some workers are of opinion that the internal friction experienced by the polar groups in their orientation is something quite different from the macroscopic viscosity and as such dimensions of the polar units obtained by using the macroscopic viscosity for η in this relation may not represent true values. But at the same time it must also be remembered that the the number of cases in which proper dimensions of the polar units have been obtained by using the macroscopic viscosity in this relation, is not quite a few. It is well known that strikingly good agreement between the observed and theoretical values were obtained in Mizushima's (1927) experiments. Since then many workers have obtained for various substances the correct values of radii of their rotating units. Race (1931), for example, calculated the dimension of polar particles in mineral oils in fair agreement with their correct values. Hartshorn and his co-workers (1940) from their study on a number of phenolic resins obtained the dimensions of the hydroxyl group, the most probable group of the resin molecule for orientation. One of us (Bhattacharya, 1944a, 1944b) also found similar results in the case of lac and some of its constituents.

Again we can write, $$\tau = \frac{\xi}{2KT'} = \frac{C\eta}{T'}$$

if it is assumed that the inner frictional torque is proportional to macroscopic viscosity.

Therefore $$\log T\tau = C' + \log \eta$$

But since $\log \eta = A + \frac{Q}{RT'}$, which may be seen from the viscosity-temperature graph in figure 8 to hold good in this case,

$$\log T\tau = C'' + \frac{Q}{RT'}$$

where Q = molar activation energy, and R = molar gas constant.

If the above assumption is true, a straight line graph is expected when $\log T\tau$ is plotted against $1/T$.

Here the relaxation time τ has been calculated from the relation

$$\tau = \frac{1}{\omega\epsilon''} \cdot \frac{\epsilon_\infty' + 2}{\epsilon_0' + 2} \{\epsilon_m'' \pm \sqrt{\epsilon_m''^2 - c''^2}\}$$

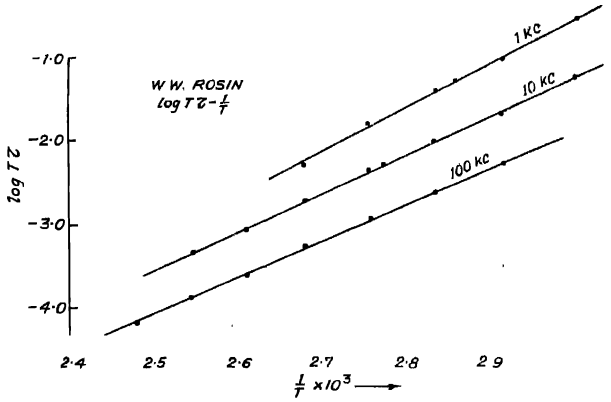

Fig. 7.

for frequencies of 1 kc/s, 10 kc/s, and 100 kc/s over the investigated range of temperature and the results of computation are tabulated in Table I.

The calculated values of log $T\tau$ for different frequencies are plotted against $\frac{1}{T}$ and the graphs are shown in figure 7. All these graphs are straight lines which justify our previous assumption.

The resistivity of an insulating material is due to lack of mobility of its charge carriers and so depends on its inner viscosity. Hence the resistivity and inner viscosity are related to temperature in a similar fashion. We find, however,

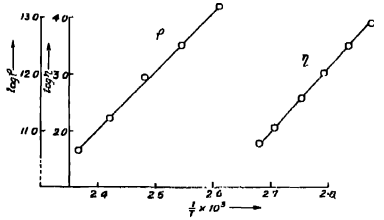

Fig. 8.

from the results of resistivity and viscosity determinations at different temperatures shown in Tables II and III respectively that the resistivity and macroscopic viscosity behave similarly with temperature. In figure 8 logarithms of both d.c. resistivity and viscosity are plotted against $\frac{1}{T}$ and it may be seen that both

the graphs are straight lines and they are almost parallel, signifying that they have almost same value of molar activation energy.

TABLE I

Frequency in kc/s	Temperature $t°C$	Temperature $T°K$	$\frac{1}{T} \times 10^3$	Relaxation time in sec	log $T\tau$
1	60°	333	3.003	9.13×10^{-4}	−0.517
	70°	343	2.915	2.70×10^{-4}	−1.003
	77°	350	2.857	1.48×10^{-4}	−1.286
	80°	353	2.833	1.21×10^{-4}	−1.369
	90°	363	2.755	4.44×10^{-4}	- 1.703
	100°	373	2.681	1.20×10^{-5}	−2.349
10	60°	333	3.003	1.62×10^{-3}	−1.208
	70°	343	2.915	5.60×10^{-5}	−1.717
	80°	353	2.833	3.06×10^{-5}	−1.961
	88°	361	2.773	1.48×10^{-5}	−2.272
	90°	363	2.755	1.28×10^{-5}	−3 323
	100°	373	2 681	5.02×10^{-6}	−2.728
	110°	383	2.611	1.85×10^{-6}	−3 150
	120°	393	2.545	1.19×10^{-6}	−3.330
100	70°	343	2.915	1.51×10^{-5}	−2.286
	80°	353	2.833	6.71×10^{-6}	−2.626
	90°	363	2.755	3.47×10^{-6}	−2.900
	100°	373	2.681	1.48×10^{-6}	−3.258
	110°	383	2.611	5.70×10^{-7}	−3.661
	120°	393	2.545	3.12×10^{-7}	−3 911
	130°	403	2.481	1.39×10^{-7}	−4 251

TABLE II

D.C. conductivity and resistivity—temperature

Temperature $t°C$	Temperature $T°K$	$\frac{1}{T} \times 10^3$	D.C. Conductivity K_0 mho-cm^{-1}	D.C. Resistivity ρ ohm-cm.	log ρ
110°	383	2.611	6.5×10^{-14}	1.54×10^{13}	13.1871
120°	393	2.545	3.16×10^{-13}	3.16×10^{12}	12.5003
130°	403	2.481	1.14×10^{-12}	8.77×10^{11}	11.9341
140°	413	2.421	5.89×10^{-12}	1.70×10^{11}	11.2299
150°	423	2.364	2.24×10^{-11}	4.46×10^{10}	10.6498

TABLE III

Viscosity—Temperature

Temperature			Viscosity	
$t°C$	$T°K$	$\frac{1}{T} \times 10^3$	η in poise	$\log \eta$
75	348	2.874	7,870	3.896
80	353	2 833	3,020	3.480
85	358	2.793	1,060	3.025
90	363	2.755	372	2.573
95	368	2.717	112	2.050
100	373	2.681	60	1.778

Hence from all these evidences it would not be very much wrong to assume that the macroscopic viscosity is the inner friction for our purpose here.

In order to obtain the dimension of the rotating unit from the relation

$$\tau = \frac{4\pi\eta a^3}{K\bar{T}}$$

we should know the value of the relaxation time τ. This may be calculated from another relation due to Debye, viz.,

$$\omega\tau = \frac{\epsilon'_\infty + 2}{\epsilon'_0 + 2}$$

at the point where the maximum dielectric loss takes place for any frequency in the loss factor—temperature (ϵ''–temp) graph, ϵ'_∞ being the value of the dielectric constant at very high frequency and ϵ'_0 is the dielectric constant at very low frequency i.e., the static dielectric constant. These values of ϵ'_∞ and ϵ'_0 are estimated from ϵ'—$\log f$ graph corresponding to a temperature at which the dielectric loss is maximum for a particular frequency f and are used in the calculation of the relaxation time τ. Now knowing the viscosity corresponding to the temperature at which the loss maximum occurs and using it in the equation

$$\tau = \frac{4\pi\eta a^3}{K\bar{T}}$$

the radius of the rotating unit can be obtained. Table IV shows the results of such calculations, from which it may be seen that the values, though computed from different data, are more or less in close agreement. The range of variation is narrow around the most probable value of 4.6Å.

TABLE IV

Calculated relaxation time and radius of the rotator

Loss maximum temperature °C	Relaxation time τ in sec	Frequency in kc/s	log η	Radius of the rotator 'a' in Å
77°	1.48×10^{-4}	1	3.80	4.55
88°	1.48×10^{-5}	10	2.78	4.60
96°	2.97×10^{-6}	50	2.10	4.55
100°	1.48×10^{-6}	100	1.78	4.65

The average dimension of the rotating unit so obtained reveals an interesting fact. The radius of the abietic acid molecule, the chief constituent of rosin, theoretically calculated from its established chemical structure is of the same order. This suggests that abietic acid molecule as a whole takes part in the orientation.

It may be mentioned here that from a similar study of the dielectric properties of a sample of wood rosin, Kitchin and Muller (1928) also obtained the dimension of the rotating unit as 4.8Å which is almost equal to the value obtained here.

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